1 432 725

PATENT SPECIFICATION (11) 1 432 725

(21) Application No. 4416/74 (22) Filed 30 Jan. 1974
(31) Convention Application No. 12299/73
(32) Filed 30 Jan. 1973 in
(33) Japan (JA)
(44) Complete Specification published 22 April 1976
(51) INT CL² B01J 13/02
(52) Index at acceptance B8C A

(19)

(54) METHOD OF FORMING MICROCAPSULE FILMS

ERRATUM

SLIP No. 2

SPECIFICATION No. 1,432,725

Page 1, line 1, (71), *after* FUJI *insert* PHOTO

THE PATENT OFFICE
25th October, 1976

ERRATA

SPECIFICATION No. 1,432,725

Page 1, line 1, (71), *after* LTD., *insert* a
Page 1, line 30, *after* and *insert* an
Page 2, line 38, *for* comtaining *read* containing
Page 4, line 9, *for* diamines *read* diamine
Page 5, line 35, *for* iliquid *read* liquid
Page 7, line 32, *for* spiroactal *read* spiroacital
Page 7, line 33, *for* wate-insoluble *read* water-insoluble
Page 8, linc 49, *after* transparent *insert* viscous
Page 11, line 49, *delete* to (second occurrence) *insert* or
Page 11, line 59, *after* density *insert* of the

THE PATENT OFFICE
15th June, 1976

A number of patents concern encapsulation by this polymerization process as disclosed, for example in Japanese Patent Publications Nos. 19574/63, 446/67,

PATENT SPECIFICATION (11) 1 432 725

1 432 725

(21) Application No. 4416/74 (22) Filed 30 Jan. 1974
(31) Convention Application No. 12299/73
(32) Filed 30 Jan. 1973 in
(33) Japan (JA)
(44) Complete Specification published 22 April 1976
(51) INT CL² B01J 13/02
(52) Index at acceptance B8C A

(54) METHOD OF FORMING MICROCAPSULE FILMS

(71) We, FUJI FILM CO., LTD., Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of forming microcapsule films.

Many methods are known for encapsulating hydrophilic materials in a polar liquid.

Such microcapsules are used for encapsulating various core materials, and they may have the following functions:

a. to store a liquid material as an apparently solid material or fine powder,
b. to modify the weight and quantity of encapsulated materials,
c. to control the time of release of the encapsulated materials,
d. to isolate reactive, materials, so that two or more reactive materials can be contained at the same time in the same system for a long period of time or encapsulated materials can be protected from external influences or stored for a desired period of time, and
e. to shield the colour, the flavour and the virulence of the materials contained.

Much research has been conducted in the use of micro-capsules in connection with recording materials, medical supplies, perfumes, agricultural chemicals, chemicals, adhesives, liquid crystal paints, foods, detergents, dyestuffs, solvents, catalysts, enzymes and rust-inhibitors. Such microcapsules have been used for containing aspirin, perfume, menthol, insecticides, rust-inhibitors (for riveting), liquid crystals, pressure-sensitive adhesives, and colour-formers in pressure-sensitive copying sheets.

Methods of encapsulating can be classified into chemical processes, physico-chemical processes and physico-mechanical processes and combinations of these processes, and are described in greater detail as follows.

As methods for microencapsulation utilizing chemical processes, an interfacial polymerization process and "in situ" polymerization process are known.

(a) Microencapsulation using an interfacial polymerization process utilizes a reaction in which a polymer is synthesized (see *Journal of Polymer Science, 60,* 299 (1950)). In this process, an interfacial polymerization reaction is utilized using a combination of a hydrophobic monomer (or a prepolymer thereof) and a hydrophilic monomer (or a prepolymer thereof). The hydrophobic monomer is added to an organic medium which has no affinity for water, and the solution is finely dispersed in an aqueous phase. Then a water-soluble or water-dispersible monomer is added to the aqueous phase, by which the polymerization reaction occurs at the water/oil interfaces, to form polymer films. Compounds used for such film-formation are polyfunctional materials which cause a polycondensation reaction or an addition polymerization reaction. Thus, the formed capsules have a polyamide, polyester, polyurethane or polyurea film.

A number of patents concern encapsulation by this polymerization process as disclosed, for example in Japanese Patent Publications Nos. 19574/63, 446/67, 771/67, 2882/67, 2883/67, 8693/67 8923/67, 9654/67 and 11344/67, and British Patents Nos. 950,443, 1,046,409 and 1,091,141. In these methods, the rate of supply of the monomers becomes reduced during formation of the capsule film and the

SEE ERRATA SLIP ATTACHED

and slip number 5

supply thereof finally stops. Consequently the resulting microcapsules generally have a thin capsule film, which is a typical semipermeable membrane.

(b) In the "in situ" polymerization process, film-forming materials are supplied to either the inside or the outside of the drops of the core material, and consequently polymerization occurs at the surface of the drops of the core material. Since most known polymerization reactions can be utilized, many kinds of capsule films can be formed thereby.

(c) A number of patents concern methods in which an oily monomer and core materials coexist, for example as described in Japanese Patent Publication No. 9168/61, British Patent No. 1,237,498, French Patent No. 2,060,818 and 2,090,862. Methods for producing a polymer film on the surface of core material by applying a film-forming material from the dispersion medium are described in British Patent No. 989,264, Japanese Patent Publication No. 14327/62 and 12380/62.

In the capsule films produced by these methods, film formation is generally not sufficiently completed, and, consequently, the porosity of the capsule films is comparatively high.

Physical methods of microencapsulating include phase-separation methods using an aqueous solution and a drying method involving drying in a liquid.

The phase separation methods which are widely used comprise separating a thick polymer phase from an aqueous solution of a water-soluble polymer. Such methods include a complex coacervation process and a simple coacervation process.

(d) Encapsulation by complex coacervation is described in U.S. Patents Nos. 2,800,457, 3,116,206, 3,687,865, 3,265,630, 3,190,837 and 3,041,289. Methods for hardening the capsule films formed are described in Japanese Patent Publications Nos. 3878/62, 3876/62, 3877/62, 12376/62, 24782/62 and U.S. Patent No. 3,401,123, wherein formaldehyde, gluteraldehyde and glyoxal are used as hardening agents. Methods utilizing simple coacervation are described in U.S. Patent No. 2,800,458, French Patent No. 1,304,891, and Japanese Patent Publication No. 7727/62, 7731/62 and 9681/62.

The capsule films formed by these coacervation methods have substantially poor resistance to water or moisture and undergo swelling or permit permeation of the contents, because they are produced from water-soluble polymer starting materials. Furthermore, low molecular weight materials can pass through the capsule films thus formed because the films are porous. Furthermore, the encapsulated materials can be extracted by alcohols, ethers or ketone solvents.

(e) The drying method comprising carrying out drying in a liquid comprises dispersing a solution of a capsule or film-forming material comtaining core materials in an encapsulating medium and volatilizing the solvent to form rigid capsule films.

This method has been described in Japanese Patent Publications Nos. 13703/67, 28744/64 and 28745/64.

The capsule films formed by this method are usually in the form of a thin semipermeable membrane. Accordingly, they have the disadvantage that low molecular weight core materials penetrate through the capsule film.

Typical methods for producing capsules and the characteristics of the capsule films formed have been described above. But, additionally, phase separation methods using an organic solvent (e.g. the methods described in Japanese Patent Publication No. 12379/62 and U.S. Patent No. 3,173,878) and drying methods comprising drying in a liquid (e.g. the methods described in Japanese Patent Specification No. 28744/64 and 28755/64) are known, but they are not satisfactory because of the thickness and the density of the capsule films.

An object of the present invention is to eliminate the technical problems of the above described encapsulation methods and to provide a method of forming capsule films having improved "protective ability" for the encapsulated materials, which is an ideal characteristic for microcapsules.

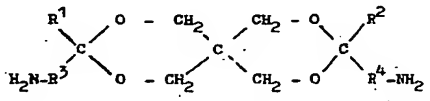
Herein, the term "improvement of protective ability" means that the density of the formed capsule film is increased that the permeability to water and resistance to light is reduced, that the degree of swelling by water or moisture is decreased and the strength is increased.

The microcapsule film obtained by the method of the present invention have low porosity, are not water-permeable, have low light-transmission, are difficulty swelled by water or moisture, and are thick and strong.

The present invention provides a method of producing microcapsule films, having decreased porosity, which comprises adding to a reaction system for

preparing microcapsule films, before or after formation of the films, a water-soluble or water-dispersible symmetric or asymmetric spiroacetal diamine or a derivative thereof, or said diamine or derivative thereof and a material which reacts with said diamine or derivative thereof to form a water insoluble material.

Examples of the preferred spiroacetal diamines are represented by the following general formula:



wherein R^1 and R^2 each represents a hydrogen atom or a lower alkyl group i.e. a group having up to 4 carbon atoms (for example, a methyl, ethyl or propyl group) and R^3 and R^4 each represents a linear or branched-chain alkylene group having 1 to 7 carbon atoms. Examples of suitable alkylene groups are methylene, ethylene, propylene, iso-propylene, butylene, pentylene, hexylene and heptylene groups. Preferred alkylene groups are straight-chain groups.

Specific examples of spiroacetal diamines represented by the above general formula include:

3,9-bis(2'-aminoethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis(2'-aminoethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-diethyl-3,9-bis-(2'-amino-ethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(2'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(4'-aminobutyl)-2,4,8,10-tetrao aspiro-(5,5)-undecane
3,9-bis-(5'-aminopentyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(1',1'-dimethyl-4'-aminobutyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(5'-aminopentyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane
3,9-bis-(6'-aminohexyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane and
3,9-(7'-aminoheptyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane.

These diamines can be easily prepared according to processes described in, for example, German Patent No. 1,092,029 and U.S. Patent No. 2,996,517.

Preferred examples of derivatives of the above compounds include (i) condensation products produced by reacting the amino groups of a diamine represented by the above formula with a compound containing at least one oxirane group, (ii) addition products produced by reacting the above diamine with acrylonitrile, (iii) reaction products produced by reacting the above diamine with urea, thiourea or guanidine, and (iv) reaction products produced by reacting the above diamine with an alkylene oxide such as ethylene oxide, propylene oxide or octylene oxide.

Compounds having an oxirane group which are a constituent of the aforesaid derivatives (i) include (a) alkyl glycidyl ethers, such as propyl glycidyl ether, butyl glycidyl ether and allyl glycidyl ether; (b) condensates of epichlorohydrin and bisphenol (e.g., Epikote 562, Epikote 812, Epikote 815, Epikote 820, Epikote 828 and Epikote 834, trade names, produced by the Shell International Chemical Co.; "Epikote" is a registered Trade Mark); (c) phenol epoxides prepared by reacting epichlorohydrin with a precondensate of a phenol resin; (d) polyglycol type epoxides prepared by reacting a polyglycol such as ethylene glycol, propylene glycol and glycerol with epichlorohydrin; (e) glycidyl esters in which the hydrogen of the carboxyl group is substituted with a glycidyl group (for example, "Kardula E" trade name, produced by the Shell International Chemical Co.); (f) an alkylene oxide such as ethylene oxide, propylene oxide, octylene oxide, epoxypolybutadiene; (g) epoxidized vegetable oil fatty acids prepared by reacting a glyceride of an unsaturated fatty acid with peracetic acid; and (h) epoxy glycerides.

The condensation products of a compound having oxirane groups and the spiroacetal diamine can be prepared according to known methods, by mixing and heating these materials in the presence or absence of a solvent to a temperature above the melting point of the spiroacetal diamine. Preferred condensates can be prepared by reaction in a system containing a spiroacetal diamine having one or more amino groups per oxiran group. The details of this process are described in Example 1 of Japanese Patent Publication No. 26097/68.

The derivative of type (ii), namely the addition products of the heterocyclic amino and acrylonitrile, can be easily produced according to known methods by heating these materials at a temperature above the melting point of the spiroacetal

diamine component or near the boiling point of acrylonitrile in the presence or absence of a solvent. The details are described in Example 1 of Japanese Patent Publication No. 2586/69. Furthermore, the reaction products (iii) of heterocyclic amines and urea, thiourea or guanidine can also be easily produced using known methods.

The Addition of the Amines.

The method of the present invention of forming microcapsule films can be applied to any microencapsulation process.

The effect caused by the spiroacetal diamines increases depending on the quantity thereof, and thus the quantity thereof added is determined on the basis of the characteristics desired. However, it is preferred that the amount of the diamine be within a range of from 1/100 to 1/2, more preferably 1/50 to 1/5% based on the weight of water immiscible material to be encapsulated.

The diamines used in the present invention are added, with agitation, to the system during any step of producing capsules or after formation of capsule films. However, in these processes it is preferred to add the diamines as follows.

a) Interfacial Polymerization Process:

The process comprises the successive steps of emulsification, dispersion, hardening and conclusion of encapsulation, and it is preferred to add the diamine during or after the dispersion step.

b) "In situ" Polymerization Process:

It is preferred to add the diamine during or after a dispersion step in the process comprising emulsification, dispersion, hardening, and conclusion of encapsulation.

c) Coacervation Process:

The process comprises the successive steps applied to an ionizable hydrophilic colloid of (1) emulsification (2) coacervation, (3) cooling to gel, (4) pre-hardening, (5) hardening, (6) conclusion of encapsulation; pre-hardening treatment is the step prior to that in which the hardening agent and an alkali are co-present in the same system). It is preferred to add the diamine during or after the cooling step (3), and especially during the pre-hardening (4).

d) Other Encapsulation Processes:

It is preferred to add the diamine after (before or during) a dispersion step.

The complex coacervation process to which this invention is especially applicable is described in detail as follows.

(1) The first step is an emulsification step in which a hydrophobic water-immiscible oil (to be encapsulated) is emulsified, optionally with the aid of a surfactant, in an aqueous solution of at least one hydrophilic colloid, e.g. gelatin, which is to be the wall material and is ionizable in water (the first sol), and subsequently admixed with an aqueous solution of a hydrophilic colloid (the second sol) having an electric charge opposite to that of the first sol. The temperature of emulsification and droplet formation is not important but must be no less than the gelation point of the colloid, preferably about 40°C in the case of gelatin. The size of the droplets formed in this step is not critical and the proportion by weight of the hydrophilic colloid can be selected as desired, because the hydrophilic colloid solution is subsequently diluted with water added in the subsequent coacervation step.

As another embodiment of this step, the water-immiscible oil can be emulsified in an aqueous solution of a mixture of hydrophilic colloids which are ionizable in water and at least one of which is positively charged. The ratio of the hydrophilic colloids employed can be varied, but it is preferred that the ratio by weight of one hydrophilic colloid (on a solids basis) to the second hydrophilic colloid of opposite charge thereto be about 1.

(2) In the second step, coacervation is brought about either by adding water to the emulsified mixture or adjusting the pH. The amount of water to be added is that which will cause coacervation, and the amount to be added can be easily selected by one of ordinary skill in the art, for example, based on the disclosure contained in U.S. Patent No. 2,800,457. Again, the temperature of the system is not limiting but should not be lower than the gelation point of the colloid(s). It is, however, preferred that the temperature of the system remain substantially constant until coacervation has been achieved. Where pH adjustment is used, the initial pH of the system and the pH change are not limiting but the final pH of the system must be no greater than the isoelectric point of gelatin, preferably from a pH of 7 to 2, for example, about 4. Suitable pH-adjusting agents can be organic

acids (e.g., succinic or acetic acid) and mineral acids (e.g., hydrochloric acid).

(3) In the third step, the coacervates are cooled to cause gelation of the colloid(s). The temperature at the beginning of the cooling step is substantially the same as that used in the coacervation step. The temperature at the completion of the cooling step should be no greater than the gelation point of the colloid(s) and generally is no lower than the freezing point of water (e.g., until about 5°C), usually about 10°C.

The rate of cooling is not important and will depend on the volume to be cooled; rapid cooling can be utilized for the gelation step.

(4) Once the coacervates have gelled, then the fourth step is carried out, wherein the pH of the system is adjusted to the alkaline side, preferably to a pH of about 7.5 to about 12; usually the final pH will be about 10. The temperature during pH adjustment to the alkaline side is not critical but should be no greater than the gelation point of the colloid. The pH can be rendered alkaline by utilizing an alkali such as sodium or potassium hydroxide. A hardening agent can be added before or after this pH adjustment or simultaneously therewith.

(5) After the addition of the hardening agent, the temperature of the coacervate may if desired be raised, for example to about 40°C to 60°C., to more effectively harden the coacervate.

The ionizable hydrophilic colloid used in this coacervation may be a natural or synthetic one such as a compound containing amino acids, for example, gelatin, casein or an alginate, a saccharide, such as gum arabic or carrageenin, a copolymer such as of styrene and maleic anhydride or styrene and methyl vinyl ether, a cellulose compound, such as carboxymethyl cellulose or cellulose sulphate, or a soluble starch such as sulphated starch.

The hydrophobic oil to be encapsulated may be a natural mineral oil, animal oil, vegetable oil or synthetic oil. Examples of mineral oils include petroleum and petroleum fractions such as kerosene, gasoline, naphtha and paraffin oil; examples of the animal oils include fish oil and lard oil; examples of the vegetable oils include peanut oil, linseed oil, soybean oil, castor oil and corn oil; examples of synthetic oils include biphenyl derivatives such as alkylated biphenyls (e.g., methyl, ethyl or isopropyl-substituted biphenyls), phosphate esters, naphthalene derivatives, phthalic acid derivatives and salicylic acid derivatives. These oils may contain solutes, e.g. colour-forming compounds, perfumes or drugs.

In order to emulsify and disperse in water the hydrophobic iliquid to be encapsulated, an anionic, cationic or non-ionic surface-active agent is preferably used to prevent phase reversal (i.e., formation of a w/o emulsion). Turkey red oil or a sodium alkyl benzene sulphonate can be utilized as this agent. Thus an oil-in-water emulsion can be obtained by (1) emulsifying a hyrophobic oily liquid in at least one aqueous solution of a hydrophilic colloid. (2) The resulting emulsion is then subjected to dilution with water and adjustment of the pH, to thereby deposit the coacervate around the emulsified individual oil droplets. (3) The coacervate deposited on the surface of the oil droplets is cooled from outside the vessel to gel the wall colloid(s) to form the film. (4) Then, in order to harden the wall film (especially of a protein), formaldehyde, dialdehyde, e.g., glutaraldehyde or glyoxal, a ketoaldehyde, e.g., methylglyoxal, or a combination of formaldehyde and a dialdehyde or a ketoaldehyde, or an oxidation product of a polysaccharide, is added to the system, before, during or after adjustment of the pH of the system to the alkaline side, e.g. sodium or potassium hydroxide or sodium carbonate, and preferably the system is heated to a temperature above room temperature (about 18°C). (5) In order to impart heat-resistance to the capsule wall film, the system is left to harden for a long period of time, for example one day, at a low temperature, for example, room temperature, or, if rapid processing is required, heated to about 40° to 60°C.

Shock Prevention.

An encapsulation process utilizing coacervation has the defect that the hardening pretreatment step takes a long time. It is beneficial to use in this process the procedure of British Patent No. 1,253,113, which improves the above defect in the present invention, because it becomes possible to change the pH to the alkaline side in a short time in a hardening pretreatment by adding "a shock-preventing agent" in the presence of the hardening aldehydes.

The term "shock" as used herein means the phenomenon in which, in carrying out the hardening pretreatment of a coacervation capsule solution containing gelatin as described in the aforesaid British Patent Specification, the

viscosity is rapidly increased when the pH of the system is at around the isoelectric point of gelatin. The term "shock-preventing agent" means a solution which prevents such shock. Shock-preventing agents which can be used in this invention are polyelectrolytes having an anionic functional group; examples thereof are (v) modified cellulose, (vi) an anionic starch derivative, (vii) an anionic acid polysaccharide, (viii) a condensate of naphthalene sulphonic acid and formaldehyde, (ix) a hydroxyethyl cellulose derivative, (x) a copolymer of vinylbenzene sulphonate, (xi) a copolymer of sodium acrylate and (xii) a copolymer of maleic acid anhydride.

As specific examples of (v) modified cellulose, there may be mentioned polysaccharides having β-1,4-glucoside bonds of glucose and having anionic functional groups. Part or all of the hydroxyl groups of the cellulose may be etherified or esterified. Illustrative of cellulose ethers are carboxymethyl cellulose, carboxyethyl cellulose and metal salts thereof, and illustrative of cellulose esters are cellulose sulphate, cellulose phosphate and metal salts thereof.

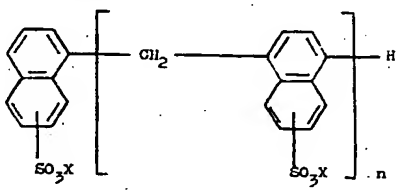
The anionic starch derivative (vi) may be one which is composed of a linear polysaccharide amylose formed by only α-1,4 bonds of D-glucose, or a branched polysaccharide amylopectin formed by mainly α-1,4 bonds of D-glucose and partially side-chain branched by α-1,6 bonds.

Examples of the above starch derivatives include carboxymethyl starch, carboxyethyl starch, starch sulphate, starch phosphate and starch xanthate; these are obtained by etherification of esterification of corn starch, wheat starch, rice starch, potato starch, sweet potato starch or tapioca starch, which may be extracted in high yield from either the seeds or the roots of the plants.

As examples of the anionic acidic polysaccharides (vii) there may be mentioned polygalacturonic acid, which is obtained by polycondensing linearly D-galacturonic acid between α-1,4 bonds thereof. The acid polysaccharide contains pectin, pectic acid and pectinic acid; these are basic substances comprising pectins and have been defined as follows: pectinic acid is polygalacturonic acid in the colloidal form containing some methyl ester groups; pectin is water-soluble pectinic acid containing methyl ester groups; and pectic acid is ollygalacturonic acid in the colloid form containing no methyl ester groups.

The separation of these compounds may be conducted, in general, by extraction from acids.

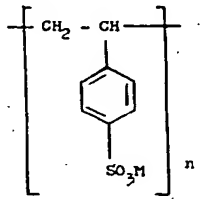
The condensate (viii) of naphthalene sulphonic acid and formaldehyde is represented by the following general formula:



wherein X is a hydrogen atom, an alkali metal or an ammonium group, and n is a positive integer. The shock-preventing ability of this condensate is influence by the degree of polymerization, and it is preferably that n be 5 to 9. In general, the larger the value of n, the more the water-solubility and viscosity increases. These compounds are described in *Kogyo Kagaku Zashi*, 66 [1], pp. 55 to 69 (1963).

As examples of the hydroxyethyl cellulose derivative (ix) there may be mentioned the carboxymethyl ether of hydroxyethyl cellulose, hydroxyethyl cellulose sulphate and hydroxyethyl cellulose phosphate.

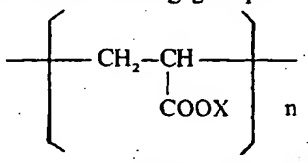
As examples of the copolymers (x) of vinylbenzene sulphonate, there may be mentioned copolymers of vinylbenzene sulphonate with acryloylmorpholine, morpholino methylacrylamide, acrylamide, vinyl pyrrolidone and methoxymethyl acrylamide. These polymers contain the following group in the molecule:



wherein M is an alkali metal and *n* is a positive integer. The amount of vinylbenzene sulphonate in the copolymer is preferably 45—95 mol percent, more preferably 60—85 mole percent, and it is preferred, for the purpose of this invention, to use a copolymer having a molecular weight of 10,000 to 3,000,000, particularly 100,000 to 1,000,000.

As examples of the copolymers (xi) of acrylic acid, there may be mentioned copolymers of acrylic acid and acryloylmorpholine, morpholino methylacrylamide, acrylamide, vinyl pyrrolidone and methoxymethyl acrylamide.

These polymers contain the following group in the molecule:



wherein X is a hydrogen atom or an alkali metal, and *n* is a positive integer. The amount of acrylic acid in the copolymer is preferably 40 to 95 mol percent, especially 50 to 85 mol percent, and it is preferable, for the purposes of this invention, to use a copolymer having a molecular weight of 6,000 to 2,000,000, especially 50,000 to 1,000,000.

As examples of copolymers (12) of maleic acid anhydride, there may be mentioned copolymers of maleic acid anhydride and an unsaturated compound having an active double bond (e.g. styrene, ethylene, methylvinyl ether or vinylacetate), salts thereof (e.g. alkali metal salts such as the sodium and potassium salts, or ammonium salts), and half-esters thereof (e.g. alkyl esters such as methyl esters and ethyl ester).

The amount of the polyelectrolyte is from 1/12 to 1/2 by weight based in the total amount of hydrophilic colloids present.

The process of the present invention is extremely useful for the production of microcapsules. It is useful to combine the present invention and those processed as described in German Offenlegungsschriftens 2,133,052 and 2,138,842 or in U.S. Patent Application Serial No. 354050/73. It is also useful to combine the present invention and those processes relating to the addition of a coacervate-inducing agent at a step prior to the completion of gelation of the coacervate, as described in, for example, OLS Nos. 2,120,922, 2,135,681 and 2,210,367.

Other Additives.

In the present invention, the spiroactal diamines can also be added together with (xiii) a compound which forms a wate-insoluble material upon reaction under the condition employed for microcapsules formation with the heterocyclic amine, such as an aldehyde, epoxy compound, alkyl halide, acid anhydride, acyl halide, polyhalohydrin or polybasic acid chloride. The aldehydes are one of the preferred additives, such as acetaldehyde, formaldehyde, glyoxal, methylglyoxal, glutaraldehyde, acrolein, 2-hydroxyadipaldehyde and dialdehyde-starch. These insoluble compounds are added in an amount of about 1/100 to about 10 times and particularly about 1/10 to about 2 times by weight of the spiroacetal amines used.

The spiroacetal diamine may also be used together with (xiv) another water-soluble or water-dispersible amine having at least one amino group, such as octyl amine, nonyl amine, dodecyl amine, stearyl amine, ethylene diamine, trimethylene diamine, 1,7-diamino-heptane, 1,9-diaminononane, 1,10-diaminodecane, N,N'-diaminopropyl piperazine, diethylene triamine, triethylene tetramine, tetraethylene pentamine *m*-hexamethylene triamine, tris-(N-aminopropyl)isocyanurate, guanidine and trimethylolmelamine, which is added in an amount below about 70% and particularly below 50% by weight of the heterocyclic amine. Thereby dense films can be formed.

The above-described additives (xiii) and (xiv) can be added separately (before or after) or simultaneously with the addition of the spiroacetal amines.

Many of the spiroacetal diamines used in the present invention have the properties that under alkaline conditions cloudiness results and they easily react with the above-described additives, resulting in their precipitation in water. Further, they are stable themselves and do not become coloured during storage; accordingly, they are very easy to use.

The invention is especially effective to modify capsule films formed from gelatin; thus surprising effects, for example, improvement in light-transmittance,

prevention of swelling by moisture, improvement in strength and an increase in density of these films can be obtained.

In the prior method for producing capsules using only aldehydes as a hardening agent, unreacted aldehydes generally remain and cause a disturbing odour. According to the present invention, these residual isolated aldehydes effectively disappear and, consequently, capsules do not have a bad odour.

Moreover, it is a very important fact in the present invention that the capsules neither coalesce nor aggregate even though the capsule films are greatly modified.

The synthesis of spiroacetal diamines and condensates thereof which can be used in the present invention is illustrated in greater detail in the following Synthesis Examples. Unless otherwise indicated, all parts, percentages and ratios given hereinafter are by weight.

SYNTHESIS 1.

6.8 g (0.05 mole) of pentaerythritol, 1 g of *p*-toluene sulphonic acid and 100 ml of toluene were mixed with 18.5 g (0.1 mols) of 5-cyanopentanal dimethylacetal. The mixture was refluxed by heating for 4 hours. The reaction mixture was filtered and the filtrate was condensed under vacuum to produce 17.9 g of 3,9-bis-(4-cyanobutyl)-2,4,8,10-tetraoxaspiro (5,5) undecane as a viscous liquid.

This viscous liquid was dissolved in 60 ml of ethanol and charged into an autoclave together with 100 ml of ethanol saturated with ammonia and 5 g of an activated (alkali-treated) Raney cobalt catalyst. Hydrogen was added at an initial hydrogen pressure of 107 kg/cm² at a reaction temperature of 120°C for 2 hours. After separating the catalyst by filtration, the filtrate was condensed and the condensate was distilled under vacuum to produce 8.2 g of a spiroacetal diamine, namely 3,9-bis-(5'-amino-pentyl)-2,4,8,10-tetraoxaspiro (5,5) undecane as a distillate having a boiling range of 217—221°C/0.2 mm Hg.

33.1 Parts by weight of the aforesaid diamine were melted by heating. Then 13.0 parts by weight of butyl glycidyl ether were added dropwise with stirring while keeping the temperature at 60°C. After addition, the mixture was stirred for an additional 2 hours. The resulting reaction condensation product was a colourless transparent viscous liquid.

SYNTHESIS 2.

13.6 g of 3,9-bis-(6'-cyanohexyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane were produced by condensing 11.9 g of 7-cyanoheptanal dimethyl acetal with 43.5 g of pentaerythritol. Then this was catalytically reduced as described in Synthesis 1 to produce 8.6 g of 3,9-bis-(7-aminoheptyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane. Melting point: 74—75°C.

386 Parts by weight of the thus resulting spiro diamine were melted at 80—85°C, and 130 parts by weight of butyl glycidyl ether were added dropwise thereto over a 1.5 hour period with stirring. After addition, the mixture was stirred for an additional 2 hours to produce colourless transparent viscous liquids.

SYNTHESIS 3.

109.6 g (0.4 mole) of 3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane (hereinafter designated ATU) were melted in a reactor equipped with a stirrer, a reflux condenser, a dropping funnel and a thermometer while keeping the temperature at 45—55°C. Then 30.0 g of phenyl glycidyl ether were added dropwise over a 2 hour period with stirring. After addition, the mixture was stirred for an additional 2 hours.

The resultant reaction mixture was a colourless transparent liquid.

SYNTHESIS 4.

27.4 g (0.1 mole) of ATU and 11.4 g (0.1 mole) of allyl glycidyl ether were reacted under the same conditions as described in Synthesis 3, to produce a liquid condensate.

SYNTHESIS 5.

27.4 g (0.1 mole) of ATU and 6.5 g (0.05 mole) of butylglycidyl ether were reacted under the same conditions as in Synthesis 3, to produce a liquid condensate.

SYNTHESIS 6.

27.4 g (0.1 mole) of ATU and 9.3 g (0.05 mole) of E Kardula (trade name, a glycidyl ester produced by the Shell International Chemical Co.) were reacted in the same manner as in Synthesis 3 to produce a liquid condensate.

SYNTHESIS 7.

274 g (1 mole) of 3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane were melted while keeping the temperature at 45°—55°C. Then, 63 g (1 mole) of acrylonitrile was added dropwise over a 1 hour period with stirring. After the addition, stirring was continued at 60°C for an additional 1 hour to stoichiometrically produce a colourless transparent viscous liquid.

The film-forming method of the present invention will be illustrated in greater detail by the following examples.

EXAMPLE 1.

Step (1): Emulsification

6 Parts of acid-treated gelatin (from pigskin) having an isoelectric point of 8.2 and 6 parts of gum arabic were dissolved in 30 parts of water at 40°C. To this solution, 0.2 parts of sodium nonylbenzene sulphonate were added as an emulsifier.

30 Parts of diisopropylnaphthalene containing 2.5% (by weight) of 3,3'-bis(*p*-dimethylaminophenyl)-6-dimethylaminophthalide, generally known as Crystal Violet Lactone ("Crystal" is a registered Trade Mark) and 2.0% (by weight) of benzoyl leuco Methylene Blue as a colour-forming oil were added to the colloidal solution with vigorous stirring to produce an oil in water (o/w) emulsion. Stirring was stopped when the oil drop size became 6—10μ.

Step (2): Coacervation

To this emulsion, 200 parts of warm water at 40°C were added. 20% hydrochloric acid was added dropwise while stirring, to adjust the pH to 4.4.

Step (3): Gelation

The mixture was cooled externally with stirring to gel the colloidal films deposited on the oil drops.

Step (4): Pre-hardening and Amine addition

When the temperature of the liquid became 10°C, 2.0 parts of a 37% formaldehyde solution were added while stirring. Then 20 parts of a 7% solution of sodium carboxymethyl cellulose having an etherification degree of 0.75 were added thereto. A solution prepared by diluting 2.0 parts of the amine condensation product was obtained by Synthesis 1 with 5 parts of water was added dropwise thereto with stirring.

Step (5): Hardening

10% solution of sodium hydroxide was added dropwise to adjust the pH to 10. The mixture was kept at 40°C for 1 hour by external warming to obtain a slurry of hardened capsules containing a colour-forming liquid.

EXAMPLE 1A.

The following Example illustrates the use of the capsules of the invention in pressure-sensitive copying paper of the type containing an encapsulated colourless compound which colour-forms upon contact (after rupture of the capsule) with an acidic material, e.g. an acid-coated paper known as a developer sheet.

Ten parts of a 10% solution of PVA—210 (a polyvinyl alcohol, average degree of polymerization 1000, degree of saponification 87%, produced by Kuraray Co.) and 3 parts of corn starch were added to 100 parts of the capsule slurry of Example 1. The mixture was coated in a dry amount of 5.5 g/m² on a sheet of paper having a weight of 50 g/m² and dried to produce a capsular coated paper.

b) A mixture prepared by adding 7 parts of a 10% solution of PVA—210 and 3 parts of corn starch to 100 parts of capsules which were produced as in Example 1 but without using the amine compound of Synthesis 1 was likewise coated on paper to produce a copying paper (Comparison 1). When the characteristics of these coated papers were compared, the results shown in Table 1 were obtained.

TABLE 1

Properties of Capsule Films	Sheets coated with Capsules of: Example 1	Comparison 1
Strengths of Capsules:	Colour Densities	
Pressure-Resistance	0.12	0.15
Friction-Resistance	0.08	0.12
Moisture-Resistance	0.30	0.40
Permeability of Capsules:		
1. With Sheet B	0.25	0.85
2. With Sheet A	0.06	0.28
3. With Dispersion A	0.08	0.24
Stability to Sunlight:		
1. Colouring forming due to Exposure:		
after Exposure of 10 Minutes	0.10	0.12
30 Minutes	0.15	0.22
2. Activity of Colour Former:		
after exposure of 0 Minute	0.95	0.94
10 Minutes	0.92	0.90
30 Minutes	0.87	0.81
60 Minutes	0.82	0.68

From these results, it can be seen that the strength, permeability of the capsule films and the moisture-resistance were remarkably improved by the addition of the amine in accordance with the invention.

Except for the item "Activity of Colour-Former", the smaller the colour density is, the more preferable the result is.

The method of testing in this and subsequent examples involved the use of two developer sheets prepared as follows.

Method of Producing Developer Sheet A:

100 Parts of activated acid clay (clay pre-treated with sulphuric acid) were dispersed by using a Kedy mill in 300 parts of water containing 6 parts of a 40% aqueous solution of sodium hydroxide and 0.5 part of sodium hexametaphosphate. To this dispersion, 4 parts of a sodium polyacrylate (produced by the Toa Gosei Chemical Industry Co. under the trade name Alon 20LL) were added. Then, 35 parts of a styrene-butadiene latex (produced by the Dow Chemical Co. under the trade name Dowlatex 636) were added thereto.

This clay dispersion A was applied to a sheet of paper having a weight of 50 g/m² by knife-coating so as to provide a layer of solids content of 8.0 g/m². Further, in order to increase the surface smoothness, the coated paper was treated by a super-calender to produce a sheet having an acidic coating and a surface smoothness of 120 seconds (measured using a Beck smoothness tester).

Method of Producing Developer Sheet B:

5 Parts of acid clay and 3 parts of agalmatolite were dispersed in 30.6 parts of water. The pH of this clay slurry was adjusted to 10 by adding 20% by weight of sodium hydroxide.

To this slurry, 0.1 parts of sodium hexametaphosphate and 0.2 parts of the sodium salt of a naphthalene sulphonic acid-formaldehyde condensate (degree of polymerization 5, molar ratio 1:1) were added. Then 5 parts of a 10% aqueous solution of gelatin having a gel strength of 56 g and an isoelectric point of 7.7 were added thereto with stirring. After slowly adding a solution of 0.7 part of zinc chloride in 10 parts of water while stirring, a solution containing 2.5 parts of 3,5-di-tert-butylsalicylic acid and 0.4 part of sodium hydroxide was slowly added thereto. Then 5 parts of the aforesaid styrene-butadiene latex Dow latex 636 were added to produce a coating solution.

This coating solution was applied in an amount of 3 g/m² (dry basis) to a sheet of paper having a weight of 50 g/m² and dried to produce an acid-coated paper, which was treated by a super-calender to produce a sheet having a smoothness of 125 seconds (measured using a Beck smoothness tester).

These two developer sheets were used by placing the acid-coated surface thereof against the capsule-coated surface of a colour-former sheet to be tested.

Methods of Testing.

Pressure-Resistance:

The capsular sheet and developer sheet were placed together and pressed for 30 seconds using a pressure of 40 Kg/cm²; the resultant colour density on the surface of the developer sheet was measured using a reflection type spectrophotometer (wave length of measurement: 605μ).

The capsular sheet and developer sheet A were placed together and the capsular paper was then moved over the other sheet by revolving the capsule paper under a pressure of 20 g/cm² at a rate of revolution of 30 r.p.m. and a line speed of 1 m/min; the colour density of the mark thus formed on the developer sheet was measured using the spectrophotometer described above.

Moisture-Resistance:

The capsule sheet and developer sheet A were placed together and pressed using a pressure of 200 g/cm². After leaving them for a period of 24 hours in an atmosphere of relative humidity 100% at 50°C, the colour density of the stains which spread out on the developer sheet from the unpressed areas was measured using the spectrophotometer described above.

Permeability of Capsule film to colour formers:

1. Developer Sheet B was put on the capsule sheet in the presence of water so that its capsule-coated surface faced the developer sheet and dried at room temperature without pressure: the colour density of the stains which had formed due to leakage of colour-former oil on the capsule sheet was measured using the spectrophotometer as described above.

2. The procedure 1 was repeated but using Developer Sheet A.

3. Developer solution A was applied to the capsular surface of the capsule sheet. After drying, the fog density of the resultant composite sheet was measured using the spectrophotometer described above.

Stability to Sunlight:

1) Colour-forming due to Exposure to light:

After exposing the surface of the capsule sheet to sunlight for 10 to 30 minutes, the colour density of the sheet was measured using the spectrophotometer described above.

2) Activity of Colour-Former after Exposure to light:

After exposing the surface of the capsule sheet to sunlight for a period of 0 to 60 minutes, the sheet was put so as to face Developer Sheet A. Then, 600 kg/cm² pressure was applied thereto to rupture the capsules, by which the contents thereof were transferred to the surface of the developer sheet. Then, the colour density of the developed image was measured using the spectrophotometer described above.

The larger the density developed image is, the less the activity of the colour former in the capsules had decreased.

EXAMPLE 2.

(1) Emulsification:

6 Parts of acid-treated gelatin (from cattle hide) having an isoelectric point of 9.2 were dissolved in 25 parts of water at 40°C. Into this solution were poured

continuously 45 parts of a colour-former oil having the following composition

Crystal Violet Lactone	0.25 part
3-Methyl-2,2'-spiro-bi-(benzo(f) chromene)	0.5 part
7-N,N-Diethylamino-3-(N,N-diethyl-amino)-fluoran	7.5 parts
Rhodamine B-(*p*-nitroanilino)-lactam	0.5 part
7-Diethylamino-2,3-dimethylfluoran	2.5 parts
Benzoyl leuco methylene blue	2.0 parts
Monoisopropylbiphenyl	70 parts
Crocin	16 parts

The mixture was agitated to produce an o/w emulsion containing emulsified drops having a drop size of 10 to 12μ.

(2) Coacervation:

The emulsion was dispersed in 150 parts of warm water at 40°C with stirring. To this dispersion, there were added with agitation 35 parts of a 10% solution of gum arabic and 10 parts of a 5% aqueous solution of the sodium salt of a styrene-maleic anhydride copolymer (Scripset 500, trade name, produced by the Monsanto Chemical Co.), so as to form microcapsules. Then 10 wt% of citric acid was added dropwise thereto to adjust the pH to 4.50.

(3) Gelation:

The mixture was cooled externally to accelerate the formation of the capsule films and the gelling thereof.

(4) Pre-hardening:

After cooling to 8°C, 0.5 parts of 40% glyoxal and 0.5 parts of 37% formaldehyde were added thereto. After mixing for 2 minutes, there was added thereto a mixture of 1 part of a 20% aqueous solution of polyacrylic acid, 6 parts of a 20% aqueous solution of a condensate of sodium methylnaphthalene sulphonate and formaldehyde (degree of polymerization 5; molar ratio 1:1) and 12 parts of a 10% aqueous solution of carboxymethyl starch (degree of etherification: 0.5). Further, 20 parts of a 20% aqueous dispersion of the compound formed by Synthesis 2 were added dropwise.

(5) Hardening:

After these additions, a 30% aqueous solution of potassium hydroxide was added thereto to adjust the pH to 9.5. The temperature of the solution was raised to 40°C by heating externally. This temperature was kept for 30 minutes to produce a slurry of capsules each containing a colour-former liquid.

EXAMPLE 2A.

(a) The resulting capsules were used for producing a pressure-sensitive paper. Ten parts of a 20 wt% aqueous solution of acetyl starch (degree of acetylization — 0.4), 1 part of a wheat starch powder having an average particle size of 18μ and 4 parts of microcrystalline cellulose, were added to 100 parts of the capsule slurry of Example 2, and the resulting mixture was applied to a paper having a weight of 50 g/m^2 in an amount of 5.5 g/m^2 (dry basis) and dried.

This coated paper yielded under pressure a black image with Developer Sheet A.

(b) The above described additives were added in the same amounts as those described in (a) above to capsules produced in Example 2 but without using the compound of Synthesis 2, and the resulted mixture was likewise applied to paper to produce a coating paper (Comparison 2).

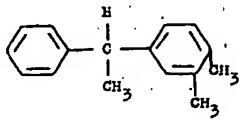
The properties of both papers are shown in Table 2. It can be seen from the results contained in this table that capsules having improved strength and decreased wall permeability are produced according to the method of this invention.

TABLE 2

Properties of Capsule Films	Example 2	Comparison 2
Strengths of Capsules:	Colour Densities	
Pressure Resistance	0.10	0.14
Friction Resistance	0.07	0.10
Moisture Resistance	0.27	0.38
Permeability of Capsules:		
2. With Sheet A	0.08	0.25
3. With Dispersion A	0.08	0.26

EXAMPLE 3.

A colour-former solution was prepared of the following composition: diphenylmethane oil of formula



30 parts containing dissolved therein

2.5% of Crystal Violet Lactone
2.0% of Benzoyl Leuco Methylene Blue and
0.5% of Rhodamin B-anilinolactam
an addition produced having residual isocyanate groups and formed from 1 mol of hexamethylene diisocyanate and 3 mols of trimethylolpropane addition product (marketed as Colonate HL by Nippon Polyurethane Industry Co.) 6 parts
polyoxypropylene polyol (marketed as Actokol 51—530 produced by Takeda Chemical Co.) 2 parts
dibutyl tin laurate. 2 parts

This oily solution was added to 50 parts of an aqueous solution containing 2 parts of carboxymethyl cellulose (approximate molecular weight 300 degree of eitherification 0.75) and 2 parts of polyvinyl alcohol (saponification degree 87%, average degree of polymerization about 500) at 20°C with stirring.

To this mixture, a solution of 1 part of the spiro amine 3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro(5,5)undecane, 5 parts of the addition compound of Synthesis 3 and 10 parts of water was added. Further, 2 parts of a 20 wt% sodium hydroxide solution were added thereto. During the above described treatment, the temperature of the system was kept at less than 20°C. Furthermore, 2 parts of 37% formaldehyde were added thereto. In order to accelerate the hardening of the wall films the temperature of the system was increased to 70°C. This temperature was maintained for 30 minutes to produce a dispersion of colour-former containing capsules having a firm capsule wall.

EXAMPLE 3A.

a) To the dispersion of capsules produced in Example 3 were added as binder 6 parts of wheat starch having a particle size of 15 and 40 parts of a 10 wt% solution of oxidized starch. The mixture was applied to a paper having a weight of 50 g/m² to form a coating of dry weight 5.0 g/m², and dried.

b) Capsules were prepared as in Example 3 but without adding 3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro(5,5)undecane, the compound of Synthesis 5 and formaldehyde. These capsules were coated as in procedure a) to produce sheets designated (Comparison 3). The results of tests thereon are shown in Table 3.

TABLE 3

Properties of Capsule Films	Example 3	Comparison 3
Strength of Capsule Film	Colour Densities	
Pressure-Resistance	0.08	0.15
Friction-Resistance	0.06	0.14
Moisture-Resistance	0.10	0.25
Permeability of Capsule Film		
1. With Sheet B	0.14	0.36
2. With Sheet A	0.06	0.15
3. With Dispersion A	0.05	0.18
Heat-Resistance of Capsule Film	100%	85%

Heat-Resistance Test for the Capsule Film:

The thermal strength of the capsule-coated paper was calculated using the following equation:

$$D_1/D_2 \times 100 = \text{Heat resistance}$$

wherein D_1 is the colour density of the developed developer sheet which results after heating the capsule-coated paper at 90°C for 10 hours, facing the surface of the capsule coating paper to the surface of the developer sheet and applying a pressure of 600 kg/cm² to rupture the capsules, and D_2 is the colour density determined likewise but without heating the capsule coated paper.

EXAMPLE 4.

A colour-former oil (designated W oil) was produced by mixing the following materials:

Santotherm 66 (hydrogenated terphenyl, produced by Mitsubishi-Monsanto Co.)	30 parts
Crystal Violet Lactone	0.5 parts
3-Methyl-2,2'-spirobi-(benzo(f) chromene)	0.5 parts
Benzoyl Leuco Methylene Blue	0.5 parts
Kerosene	5 parts

5 Parts of polymethyl methacrylate and 1 part of Colonate L (commercial name; tolylene diisocyanate-trimethylolpropane addition product, produced by Nippon Polyurethane Industry Co.) were dissolved in 15 parts of methylene chloride. To this solution, the just-described W oil was added. The temperature was kept to 16—18°C.

The W oil was emulsified in an aqueous solution of 4 parts of gum arabic, 2 parts of polyvinyl alcohol (PVA—210) described in Example 1A) and 30 parts of water using a homogenizer having a high shearing force to produce an o/w emulsion having an average drop size of 15μ. The temperature during emulsification was kept at 18—20°C. The emulsion was then added to 100 parts of water.

To the resultant mixture 3 parts of the compound of Synthesis 4 and 25 parts of a 10% aqueous solution of dialdehyde starch were added, and further 5 parts of a 20% aqueous solution of hexamethylenediamine was added thereto.

The temperature of the mixture was increased to 70°C by heating externally with stirring. This temperature was kept for one hour to conclude the encapsulation.

The resulting capsules had a heat-resistance of 95% and good strength. They were useful for producing a pressure-sensitive copying paper.

EXAMPLE 5.

25 Parts of dibutyl maleate were emulsified in an aqueous solution of 5 parts of polyvinyl alcohol (average degree of polymerization: about 1000, saponification degree: 97%), 5 parts of the sodium salt of carboxymethyl cellulose (as described in Example 3) and 45 parts of water to produce an o/w emulsion having an average drop size of 15 to 20μ.

The above resulting emulsion was added to 100 parts of water at 30°C. 20 parts of 35 wt% zirconium ammonium carbonate and 5 parts of 50 wt% urea were then added thereto with stirring. The temperature was increased to 50°C. The mixture was kept at this temperature for one hour, and then it was cooled to 25°C. Then 3 parts of the addition compound of Synthesis 4, 5 parts of a 50 wt% aqueous solution of tetraethylenepentamine, 1 part of adipic acid and 2 parts of a 37 wt% aqueous solution of formaldehyde were added thereto. The temperature was increased again to 65°C. The mixture was kept at this temperature for one hour to conclude the encapsulation.

The resulting capsules were spray-dried to produce a powder consisting of encapsulated dibutylameate.

EXAMPLE 6.

A perfume oil was prepared from 10 parts of orange perfume and 15 parts of trioctyl trimellitate.

This perfume oil was emulsified in an aqueous solution of 2 parts of the sodium salt of carboxymethyl cellulose (as described in Example 3), 3 parts of gum arabic and 30 parts of water to produce an o/w emulsion having an average drop size of 20 to 30μ. 100 Parts of water at 20°C were added with stirring. Then 20 parts of U-Ramin P-1800 (trade name; a cation-type modified urea resin, produced by Mitsui Toatsu Chemicals Inc.), 2 parts of the compound of Synthesis 6, 10 parts of a 10 wt% guanidine sulphate and 2 parts of 37 wt% aqueous solution of formaldehyde were added thereto.

Further, 20 wt% potassium hydroxide was added dropwise thereto to adjust the pH to 11.

The temperature was gradually increased to 60°C by heating externally while stirring slowly. The mixture was kept at this temperature for 24 hours.

To the resulting orange perfume capsule solution, 30 parts of a 20 wt% aqueous solution of polyvinyl alcohol (saponification degree: 87%, average degree of polymerization: about 1000) and 7 parts of corn starch were added to make a perfume ink. A paper support was printed with this ink using the silk screen process. When the printed parts were rubbed with a finger, they gave out an intense orange scent.

Furthermore, when the capsules were broken by pressing the printed surface after the printed paper support was hung on a wall for a week, they gave out an orange scent. Thus, it can be seen that the capsules produced by the method of the present invention have an excellent perfume preservability.

EXAMPLE 7.

7.5 Parts of Epikote 834 (trade mark; an epoxy resin, produced by Shell Chemical Co.) were dissolved in 20 parts of toluene. An aqueous solution of 1 part of polyvinyl alcohol (average degree of polymerization: 1000 saponification degree: 87%), 3 parts of carboxymethyl cellulose of approximate molecular weight 300; degree of etherification 075) and 25 parts of water were emulsified in the above toluene solution to produce an o/w emulsion having an average drop size of 10 to 15μ. To this emulsion, 50 parts of water at 20°C were added and then 2 parts of diethylaminopropylamine, 2 parts of the addition compound of Synthesis 7 and 1 part of 37 wt% formaldehyde were added thereto. To this mixture, 10 wt% sodium hydroxide was added to adjust the pH to 10.0. The temperature of the solution was increased to 60°C. The mixture was kept at this temperature for 24 hours while stirring.

As the result of carrying out the heat-resistance test at 50°C for 24 hours, toluene did not decrease in the resulting toluene-containing capsules.

EXAMPLE 8.

6 Parts of acid-treated gelatin (from whale) having an isoelectric point of 8.8, 4 parts of gum arabic and 0.5 parts of carboxymethyl starch (degree of etherification: 0.4, raw material: potato starch) were dissolved in 30 parts of water at 40°C. A liquid crystal composition consisting of 3 parts of methoxybenzylidene-*p*-*n*-butylaniline, 5 parts of cholesteryl chloride, 30 parts of cholesteryl nonylate and 4 parts of cholesteryl cinnamate was emulsified in the above solution to produce an o/w emulsion having an average drop size of 6 to 25μ. To the resulting emulsion, 175 parts of water at 35°C were added, and then 1 part of a phenol resin (a resorcinol modified phenol-formaldehyde resin, resin content: 60%) was added thereto. Further, a 10 wt% aqueous solution of adipic acid was added dropwise thereto to adjust the pH to 4.45. It was cooled to 8°C externally to accelerate the deposition of the colloid and the gelling thereof with the stirring being continued.

15 Parts of a 10 wt% solution of the sodium salt of carboxymethyl cellulose (degree of etherification: 0.78) were added thereto. After 1 part of 25 wt% glyoxal and 0.5 parts of 37 wt% formaldehyde were added, the pH of the mixture was adjusted to 10.0 by adding 10 wt% sodium hydroxide.

To the mixture, 3 parts of a 50 wt% aqueous dispersion of the addition compound of Synthesis 2 were added. The temperature of the mixture was increased to 40°C to produce a containing slurry of capsules liquid crystals.

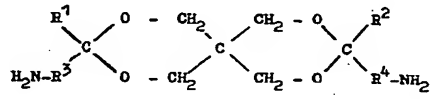
To this slurry, 4 parts of corn starch (average particle size: 15 to 20μ), 4 parts of wheat starch (average particle size: 25 to 35μ) and 10 parts of a SBR latex (styrene-butadiene rubber) were added.

A biaxial stretched polystyrene film support was surface treated by corona discharging to give a water contact angle of about 60°C. Then the above described capsule slurry was applied thereto and dried to form a capsular layer.

WHAT WE CLAIM IS:—

1. A method of producing microcapsule films, having decreased porosity, which comprises adding to a reaction system for preparing microcapsule films, before or after formation of the films, a water-soluble or water-dispersible symmetric or asymmetric spiroacetal diamine or a derivative thereof, or said diamine or derivative thereof and a material which reacts with said diamine or derivative thereof to form a water insoluble material.

2. A method as claimed in Claim 1, wherein said spiroacetal diamine is represented by the following general formula:



wherein R^1 and R^2 each represents a hydrogen atom or an alkyl group of up to 4 carbon atoms and R^3 and R^4 each represents a linear or a branched chain alkylene group having 1 to 7 carbon atoms.

3. A method as claimed in Claim 2, wherein said spiroacetal is 3,9-bis-(2'-aminomethyl)-2,4,8,10-tetraoxaspiro-(5,5)undecane, 3,9-bis-(2'-aminoethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-diethyl-3,9-bis-(2'-aminoethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(2'-aminoethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(3'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(2'-aminopropyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(4'-aminobutyl)-2,4,8,10-tetraoxaspiro-(5.5)-undecane, 3,9-bis-(5'-aminopentyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(1',1'-dimethyl-4'-aminobutyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis(5'-aminopentyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane, 3,9-bis-(6'-aminohexyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane or 3,9-(7'-aminoheptyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane.

4. A method as claimed in Claim 1, wherein said derivative is a condensation product of a diamine as defined in Claim 2 or 3 with a compound containing at least one oxirane group.

5. A method as claimed in Claim 4, wherein said compound having an oxirane group is an alkyl glycidyl ether, a condensate of epichlorohydrin and bisphenol, a phenol epoxide comprising the reaction product of epichlorohydrin with a phenol resin precondensate, a polyglycol epoxide comprising the reaction product of a polyglycol with epichlorohydrin, a glycidyl ester, an alkylene oxide, epoxy polybutadiene, an epoxidized vegetable oil or an epoxy glyceride.

6. A method as claimed in Claim 1, wherein said derivative is an addition product produced by reacting a diamine as defined in Claim 2 or 3 with acrylonitrile, a reaction product produced by reacting said amine with urea, thiourea or guanidine, or a reaction product produced by reacting said amine with an alkylene oxide.

7. A method as claimed in any preceding claim, wherein as well as said spiroacetal diamine or derivative thereof, there is included in the reaction system at least one compound which forms a water-insoluble material by reacting under the conditions employed with said spiroacetal diamine or derivative thereof.

8. A method as claimed in Claim 7, wherein said compound is an aldehyde, epoxy compound, alkyl halide, acid anhydride, acyl halide, polyhalohydrin or polybasic acid chloride.

9. A method as claimed in Claim 7 or 8, wherein said aldehyde is acetaldehyde, formaldehyde, glyoxal, methylglyoxal, glutaraldehyde, acrolein, 2-hydroxyadipaldehyde or dialdehyde starch.

10. A method as claimed in Claim 7, 8 or 9, wherein said compound is added in an amount of 1/100 to 10 times by weight per weight of the spiroacetal diamine used.

11. A method as claimed in Claim 10, wherein said compound is added in an amount of 1/10 to 2 times by weight per weight of spiroacetal diamine.

12. A method as claimed in any preceding claim, wherein a water-soluble or water-dispersible amine having at least one amino group, other than said heterocyclic amine, is included in the reaction system together with said spiroacetal diamine.

13. A method as claimed in Claim 12, wherein said water-soluble or water-dispersible amine is octylamine, nonyl amine, dodecyl amine, stearyl amine, ethylene diamine, trimethylene diamine, 1,7-diaminoheptane, 1,9-diaminonane, 1,10-diaminodecane, N,N′-diaminopropyl piperazine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, *m*-hexamethylene triamine, tris-(N-aminopropyl)isocyanurate, guanidine or trimethylolmelamine.

14. A method as claimed in Claim 12 or 13, wherein said water-soluble or water-dispersible amine is used in an amount of less than 70% by weight of said spiroacetal diamine.

15. A method as claimed in Claim 14, wherein said water-soluble or water-dispersible amine is used in an amount of less than 50% by weight of said spiroacetal diamine.

16. A method as claimed in any one of the preceding claims, wherein said spiroacetal diamine or derivative thereof is used in a complex coacervation process which comprises the steps of: (1) emulsifying a water-immiscible oil in an aqueous solution of a at least one hydrophilic colloid ionizable in water (the first sol) and admixing an aqueous solution of a hydrophilic colloid (the second sol) having an electric charge opposite to that of the first sol, or emulsifying a water-immiscible oil in an aqueous solution of hydrophilic colloids which are ionizable in water and at least one of which is positively charged; (2) adding water thereto or adjusting the pH thereof to cause coacervation, thus obtaining coacervate wherein a complex colloid is adhered to the individual oil droplets; (3) cooling the coacervate to cause gelation thereof; (4) adding a hardening agent before or after adjusting the pH of the mixture to the alkaline side; and (5) allowing the gelled coacervate to harden.

17. A method as claimed in Claim 16, wherein the hardening step (5) is carried out at an elevated temperature.

18. A method as claimed in Claim 16 or 17, wherein the spiroacetal diamine is added during or after the cooling step (3), at a temperature below the gelling point of an ionizable hydrophilic colloid.

19. A method as claimed in Claim 18, wherein the spiroacetal diamine is added at the step (4).

20. A method as claimed in any of Claims 16 to 19, wherein the hydrophilic colloid which is the capsule-forming material is gelatin.

21. A method as claimed in any of Claims 16 to 19, wherein the hydrophilic colloid which is the capsule-forming material is casein, an alginate, a saccharide, gum arabic, carrageenin, a copolymer of styrene and maleic anhydride or of styrene and methyl vinyl ether, carboxymethyl cellulose or cellulose sulphate or a sulphated starch.

22. A method as claimed in any preceding claim, wherein the microcapsule formed encapsulates a colour-forming liquid.

23. A method as claimed in Claim 5, wherein the condensation product is prepared by a method substantially as hereinbefore described in any of the Syntheses Nos. 1 to 7.

24. A method as claimed in any preceding claim, substantially as hereinbefore described in any of the Examples Nos. 1 to 8.

25. Microcapsules made by a method as claimed in any preceding claim.

26. Pressure-sensitive copying paper having a coating comprising a layer of microcapsules containing a colour-forming liquid, made by a method as claimed in any preceding claim.

27. Pressure-sensitive copying paper as claimed in Claim 26, substantially as hereinbefore described with reference to Example 1A, 2A or 3A.

GEE & CO.,
Chartered Patent Agents,
Chancery House,
Chancery Lane,
London WC2A 1QU.
— and —
39 Epsom Road,
Guildford,
Surrey.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.